Application of Electro-Chemical Techniques for the Effective Recovery of Pure Metals from E-Waste

Manish Kumar jha, Pankaj Kumar Choubey, Rekha Panda
Metal Extraction & Recycling Division, CSIR-National Metallurgical Laboratory
Jamshedpur, PIN 831 007, INDIA

*Corresponding Author:
E-mail address: mkjha@nmlindia.org ; (M.K. Jha), FAX +91-657-2345213

Abstract: In process metallurgy, the purity of metal product is always of high concern. The challenge is also due to its various applications and vast differences in the prices of pure and impure metals. At CSIR-NML, a number of hybrid electro-chemical technologies for E-waste (electronic waste) recycling have been developed. In the process development for recycling of the e-waste, devices are dismantled, classified and pre-treated to get enriched mixed metallic fractions. Further, it is treated using pyro-/hydro-metallurgical techniques to get metal ingot/metallic solution. Finally, pure metals are obtained by using electro-chemical techniques.

Keywords: E-waste; Leach Liquor; Electro-winning; Cementation; Metals

1. Introduction

Due to rapid industrialization and technological advancement, the old electrical and electronic devices have been replaced with advanced ones, resulting in the generation of massive amount of discarded electronic waste (e-waste). The discarded electronic devices are a complex mixture of various types of metals (copper, nickel, cobalt, lithium etc.), plastics, ceramics, etc. [1]. According to the report of Global e-Waste-Monitor 2020, 53.6 million metric tons (Mt) of e-waste was generated worldwide in the year 2019, and only 17.4% of it was formally collected and recycled [2].

Therefore, e-waste recycling is gaining importance in order to reduce the load on environment as well as landfill sites. E-waste recycling not only involves the recovery of metals but also involves the other factors. It is also important to note that as e-waste is heterogeneous in nature, a single recycling approach cannot be applied to all e-waste. Feasibility of e-waste recycling processes mainly depends on the negligible discharge of toxic and hazardous substances strictly adhering to economics and viability of the operational cost.

Various methods have been used for the processing of e-waste containing multiple metal ions which poses great challenges for the selective and efficient recovery of metals in pure forms. Among all approaches, electrochemical processes (electro-deposition/ electro-winning) leads to selective recovery of metal with reduced solvent and energy consumption from the solution of e-waste [3–7]. The methods, electro-winning as well as electro-refining are the primary methods used for metal purification, from solution containing a high metal concentration, at the industrial scale. Moreover, the electrochemical method leads to reduction in environmental pollution [8-10]. Electro-deposition uses the selective reduction potential of metal ion, where constant potential is applied to electrode surfaces immersed in electrolyte solution, to reduce metal ions. Moreover, at large scale, conducting electro-deposition in an aqueous electrolyte is mostly preferred due to the use of cost effective solvent i.e. water, the lesser environmental hazards compared to solvent-based electrolyte solution.

The efficient electro-chemical extraction of pure metals from the leach liquor of e-waste is highly dependent on the quality and uniformity of metal ions. The presence of multiple metal ions in the leachate is an inevitable challenge as wide range of metals with diverse properties are present in the solution. Therefore, in order to improve the quality as well as

purity of metal electro-deposition, leach liquor with multiple metal ions are processed chemically to obtain purified individual metal ions. Moreover, electro-chemical approaches for the recovery of metals have several advantages *viz.* uniform metal deposition, easy to control, cost effective, high purity product and faster processing time. Electrodeposition can also be applied over the surface of non-uniform electrode.

Keeping in view of the above factors, electro-chemical approaches have been used for the recovery of high purity metals from leach liquor of various e-wastes. Most of the reported research work on e-waste recycling are related to the separation of plastic/ metals as well as various metals in the form of pure solution and salts. The present paper reports the novel process for selective recovery of Cu, Ni, Co and Mn from discarded printed circuit boards (PCBs) and spent lithium ion batteries (LIBs) using mechanical pre-treatment followed by hydro and electrometallurgical extraction of metals. Printed circuit boards were depopulated to separate the small electronic devices and thereafter crushed mechanically to get the metallic fraction of e-waste. The fine crushed fraction of e-waste undergoes gravity separation to separate the metallic and non-metallic fraction. Similarly, LIBs were also pre-treated to get the black mass for extraction of manganese and cobalt including Cu and Ni. Further, hydrometallurgical studies were carried out to get the pure solution of Cu, Ni, Co and Mn. Subsequently, electro-winning experiments were carried out at various experimental conditions such as feed concentration, temperature and reaction time to deposit the metals at the cathode. The electrolytic grade of pure metals was produced by this electro-chemical process.

2. Experimental

2.1. Materials & Methods

The PCBs and LIBs present in discarded electronic devices i.e. e-wastes were used as the starting material. Initially, 10 Kg of PCBs and LIBs were pre-treated mechanically to get enriched metallic concentrate containing Cu, Ni, Co, Mn, etc., which were further leached in sulfuric acid to get the metals into solution. The leach liquor containing 20-30 g/L Cu, 2-3 g/L Ni, 15-20 g/L Co and 8-10 g/L Mn was further purified using solvent extraction and precipitation process to get purified and concentrated solution of individual metals. Solvent extraction experiments were carried out using LIX 84 (2-hydroxy-5-nonylacetophenoneoxime in a mixture with a small amount of 5-dodecyl-salicylaldoxime) (supplied by Henkel India Pvt. Ltd.) as an extractant at organic to aqueous ratio (O/A) 1/1 at desired equilibrium pH to separate the copper and nickel. The metals content in the solution was analyzed using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES, VISTA–PMX, CCD Simultaneous, Make Australia). Subsequently, the purified solutions of metals were concentrated by the process of evaporation and thereafter processed for recovery of metals by electro-winning process using titanium as cathode and lead as anode material while DC power supply used for applying the certain current. Electro winning is the electro-deposition of metals (Cu, Ni, Mn and Co) on cathode by applying desired current. The copper, nickel and cobalt metal sheet was deposited on cathode on applying of desired current using DC rectifier. Fig. 1 and 2 (a and b) presents the general flow-sheet for the recovery of metals from e-wastes.

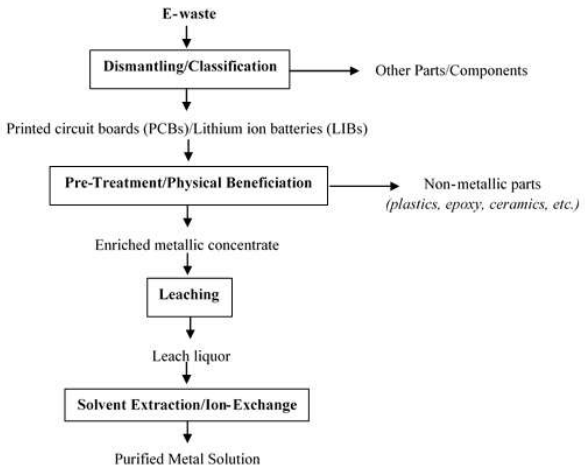


Fig. 1: Process flow-sheet to recover metals from e-wastes as purified solution.

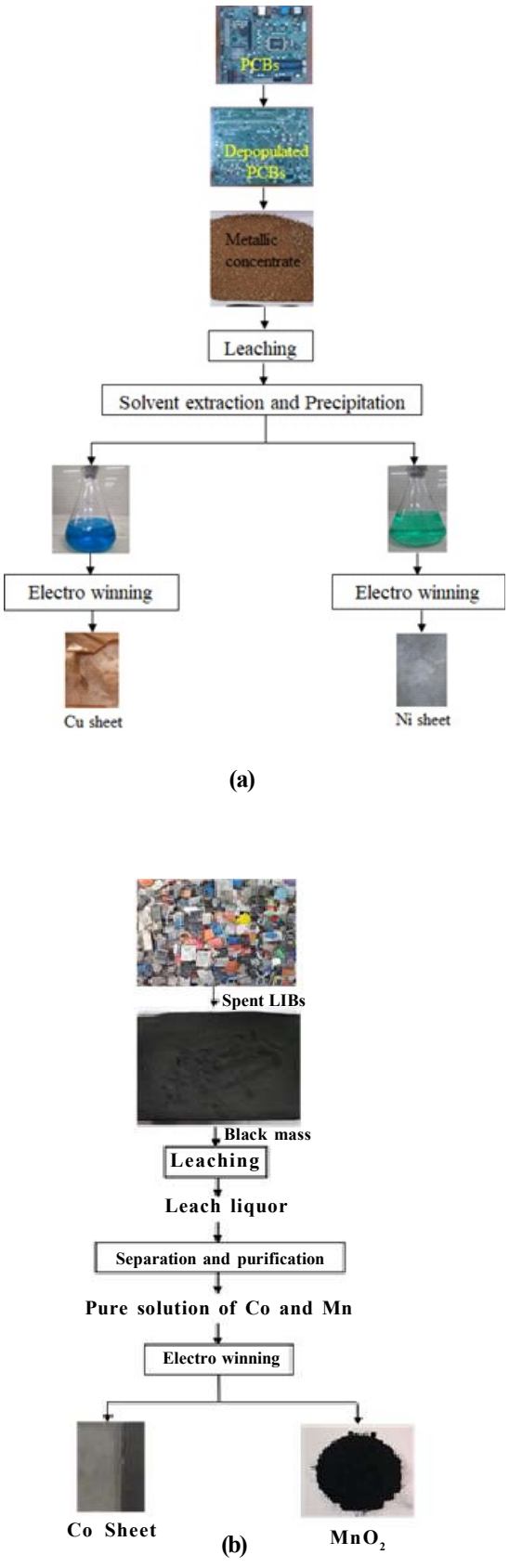


Fig. 2: Typical process flow-sheet for recovery of (a) copper, nickel and (b) cobalt and manganese from e-waste.

3. Results and discussion

The purified solution of e-waste containing Cu, Ni, Co and Mn were used for the deposition of metals at cathode using different process parameters such as feed concentration, current density, time etc., to make the reference grade materials avoiding any impurities as discussed below.

3.1. Electro-winning of Cu from leach liquor of PCBs concentrates

3.1.1. Effect of current density

Electro-winning of copper was conducted by varying the applying current density from 50 to 200 A/m^2 at room temperature. Fig. 3 shows that current efficiency increased with increase in applying current density. 94% current efficiency was found for copper deposition at an applied current density of 200 A/m^2 and thereafter the increase in current density did not have significant effect on copper electro-deposition. Therefore, 200 A/m^2 has been chosen as optimum current density for copper deposition.

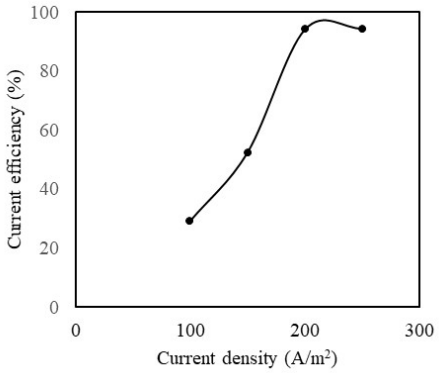


Fig. 3 Effect of current density on electro-winning of Cu metal from leach liquor [Solution: Leach liquor of PCBs containing 60 g/L Cu; Time 6 hours, Current density 100 to 250 A/m^2]

3.1.2. Effect of copper concentration

Due to heterogeneous nature of e-waste in view of metal composition, copper concentrations were found to be varied between 30-80 g/L for the leaching of PCBs concentrate in sulfuric acid (10% v/v) at various solid to liquid ratio and purification by the solvent extraction. Therefore, initial concentrations of copper in various set of electro-winning experiments were varied. The result (Fig. 4) shows

that current efficiency increases with increase in copper concentration due to abundant availability of copper ions in the solution with respect to applied current density. However, current density remarkably decreased when initial concentration of copper was found less than 45 g/L. This occurs due to the release of relatively higher amount of hydrogen ions. Therefore, 60 g/L Cu concentration in the feed solution has been considered as the optimum concentration of ions for electro-winning of copper from leach liquor of e-waste. The concentration of Cu in solution was maintained by adding the copper sulfate pentahydrate in particular interval. The electro-chemical reaction for copper deposition at cathode is presented in equations 1-3.

$$Cu^{2+} + 2e^- = Cu \qquad At\ Cathode \qquad (1)$$

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad At\ Anode \qquad (2)$$

$$2CuSO_4 + 2H_2O \rightarrow 2Cu + 2H_2SO_4 + O_2 \qquad Overall\ reaction \qquad (3)$$

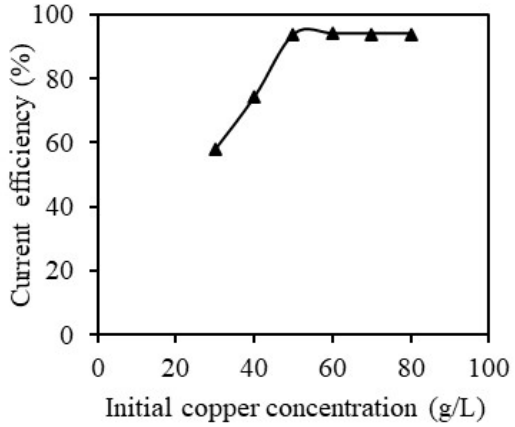


Fig. 4 Effect of concentration (Cu) on electro-winning of Cu metal from leach liquor [Solution: Leach liquor of PCBs containing 30- 80 g/L Cu and 10% H_2SO_4; Time 6 hours, Current density 200 A/m^2]

3.2. Electro-winning of Ni from leach liquor of PCBs concentrate

3.2.1. Effect of current density

Purified enriched leach liquor of Ni was used for the electro-winning. The purified solution of Ni was obtained using solvent extraction techniques by using LIX 84. Electro-winning of nickel was conducted by varying the current density from 50 to 250 A/m^2 at 60 ^oC and 60 g/L Ni concentration in feed. It was found (Fig. 5) that current efficiency increases with increase in applying current density. 91.9% current efficiency was found for nickel deposition at applying current density of 201 A/m^2 between pH 3 to 3.2 and thereafter increase in current density has no significant effect on nickel deposition. Hence, 201 A/m^2 has been considered as optimum current density for nickel deposition. Current efficiency for each set of experiments presented in Fig. 5, which was found satisfactory at optimum conditions. Accuracy was checked and found the error ~0.02%, which is satisfactory.

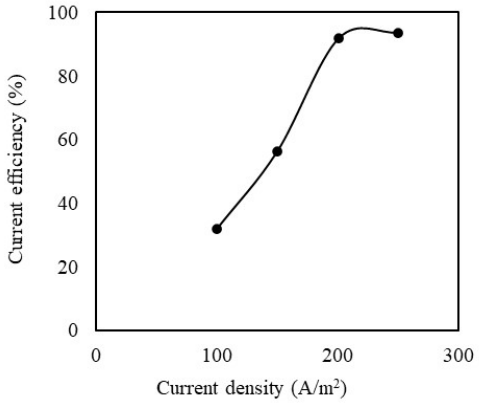


Fig. 5 Effect of current density on electro-winning of Ni metal from leach liquor [Solution: Leach liquor of PCBs containing 50 g/L Ni; pH: 3.2-3.8; Time 7 hours, Current density 100 to 250 A/m^2]

3.2.1. Effect of nickel concentration

The obtained leach liquor of PCBs concentrate containing 2-3 g/L Ni was evaporated to increase the Ni concentration in the range of 30 to 80 g/L for recovery of Ni by electro-winning process. Experiments carried out with by varying the nickel concentration from 30 to 80 g/L to electro-won the nickel at cathode. The result (Fig. 6) shows that current efficiency was increased with increase in nickel sulfate concentration due to abundant availability of nickel ions in the solution. However, current density remarkably decreased when concentration of nickel was found to be less than 40 g/L due to release of relatively higher amount of hydrogen ions. Therefore, 50 g/L Ni concentration has been considered as minimum required concentration for electro-winning of nickel from leach liquor. The electro-chemical reaction for nickel electro winning at cathode is presented in equations 4-6.

$$Ni^{2+} + 2e^- = Ni \quad \text{At Cathode} \quad (4)$$

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \quad \text{At Anode} \quad (5)$$

$$2NiSO^+_4 + 2H_2O \rightarrow 2Ni + 2H_2SO_4 + O_2 \quad \text{Overall reaction} \quad (6)$$

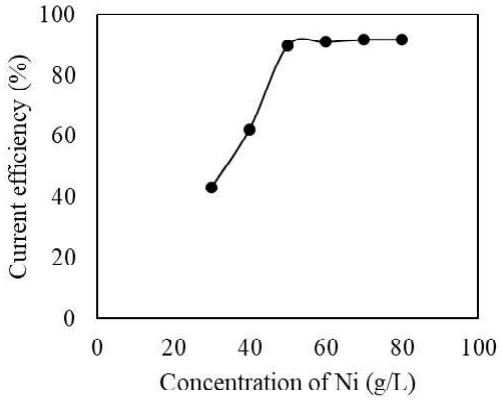


Fig. 6 Effect of concentration on electro-winning of Ni metal from leach liquor [Solution: Leach liquor of PCBs containing 30-80 g/L Ni; pH: 3.2-3.8; Time 7 hours, Current density 201 A/m^2]

3.3. Electro-winning of cobalt from leach liquor of LIBs

Electro-winning of cobalt was conducted in a beaker (capacity: 2 L, surface area of cathode: 1.2 m^2) by varying the concentration from 30 to 80 g/L at 70 °C on applying current density of 206 A/m^2 while maintaining pH 4 to 4.2 using H_2SO_4. It was found (Fig. 7) that current efficiency of cobalt deposition increases with increase in cobalt concentration due to abundantly available cobalt ions in the solution. However, current density remarkably decreased when concentration of cobalt was less than 40 g/L. This may be due to the release of relatively higher amount of hydrogen ions. Hence, 50 g/L Co concentration has been considered as the optimum concentration for electro-winning of cobalt from leach liquor of spent LIBs. The electro-chemical reaction for the recovery of cobalt sheet at cathode is shown in equations 7-9.

$$Co^{2+} + 2e^- = Co \quad \text{At Cathode} \quad (7)$$

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \quad \text{At Anode} \quad (8)$$

$$2CoSO_4 + 2H_2O \rightarrow + 2Co + 2H_2SO_4 + O_2 \quad \text{Overall reaction} \quad (9)$$

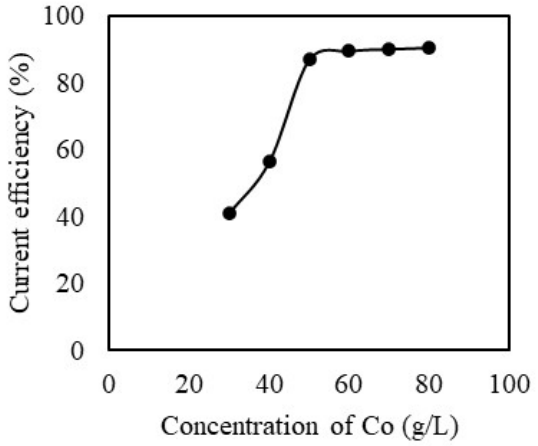


Fig. 7 Effect of Co concentration of electro-winning of Co metal [Solution: Leach liquor of LIBs, Temperature: 60 °C; pH: 4-4.2, Time 8 hours, Current density 206 A/m^2]

3.4. Electro-winning of manganese from leach liquor of LIBs

Electro-winning of Mn was carried out from the leach liquor of spent LIBs containing 35 to 75 g/L Mn to recover the manganese in the form of manganese dioxide in sulfate media. Result (Table 1) shows that 99.9% pure manganese was recovered as MnO_2 at anode due to the change of its lower oxidation state (Mn^{2+} and Mn^{3+}) to higher oxidation state (Mn^{4+}, MnO_2) [11] in 12 hours at 65 °C maintaining current density at 160 A/m^2. The current efficiency of Mn deposition was also calculated and found to be more than 90%. The electro-chemical reaction for electrolytic manganese dioxide (MnO_2) deposition at anode is presented in equations 10-12.

$$Mn^{2+} + 2H_2O = MnO_2 + 4H^+ + 4e^- \quad \text{At Anode} \quad (10)$$

$$2H^+ + 2e^- = H_2 \quad \text{At Cathode} \quad (11)$$

$$Mn^{2+} + 2H_2O \rightarrow MnO_2 + 2H^+ + H_2 \quad \text{Overall reaction} \quad (12)$$

Table 1 Electro-winning of Mn from leach liquor of LIBs

Time	Current Efficiency (%)	Energy Consumption (E.C)kWh/kg	Metal(g)	Purity%
4h	99	2.15	29.5	99.99
8h	93	2.2	41.8	99.99
12h	87	2.3	56.6	99.99

4. Electro-refining of copper

PCBs of e-waste were pre-treated using thermal techniques to get the copper anode like materials for recovery of copper by electro winning. Meanwhile, mechanical pre-treatment followed by flotation and smelting were also used to get the copper anode for recovery of pure copper metals. The impure copper was used as anode while pure copper was deposited on cathode to recover the pure copper at cathode by the process of electro-refining in presence of ionizable (H_2SO_4 and $CuSO_4$) electrolyte. During the electrolysis, precious metals like silver, gold, palladium did not dissolve in the sulfuric acid and instead deposited as anode slime. The precious metals collected anode slime could be treated hydro-metallurgically for the recovery of precious metals (Fig. 8).

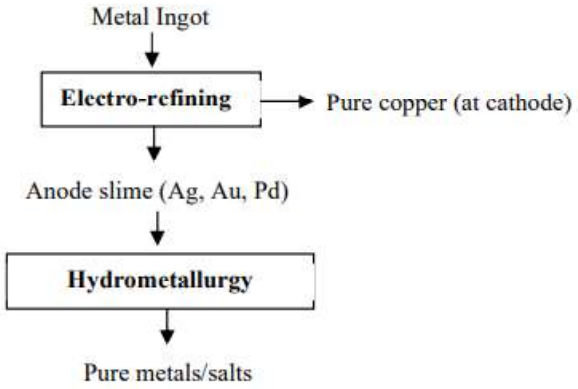


Fig. 8: Electro-refining of copper from PCBs of e-waste

5. Cementation of copper from leach liquor of e-waste

Cementation is a type of precipitation reaction in which more reactive metal dissolves in a solution to precipitate a less reactive metal from the solution. The process is often used to refine leach solutions based on the reactivity of metals. For example, aluminum or zinc can be added to a gold cyanide solution to cementate out gold. Table 2 show that Al and Zn are placed high in the electrochemical series (greater oxidation potential), while Au is placed toward the bottom (low oxidation potential). Therefore, Al and Zn are able to cement out the gold from the cyanide solution. Similarly, iron rod was also used for the cementation of copper from leach liquor of PCBs of discarded personal computer and other electronic devices. Finally, a process flow sheet was developed for the recovery of Cu, Ni, Co, Mn from e-waste and is presented in Fig. 9.

Table 2 Reactivity series of metals [12]

Reactivity series of metals			
	Potassium	K	**(Most reactive metals)**
	Calcium	Ca	
These metals are more reactive than hydrogen	Magnesium	Mg	
	Aluminum	Al	
	Zinc	Zn	
	Iron	Fe	
	Tin	Sn	
	Lead	Pb	
	Hydrogen	[H]	
These metals are less reactive than hydrogen	Copper	Cu	
	Mercury	Hg	
	Silver	Ag	
	Gold	Au	**(Least reactive metals)**

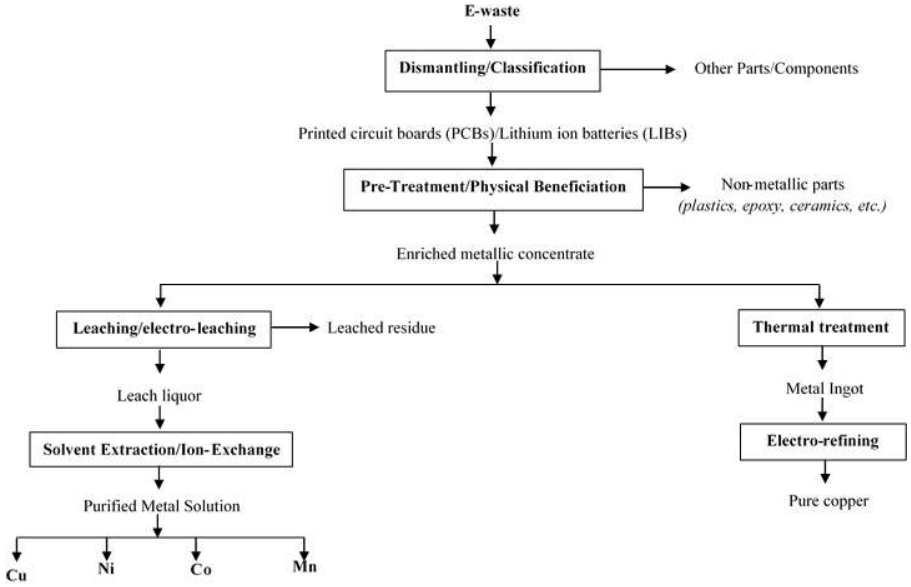


Fig. 9: Generalized process flow-sheet for the recovery of metals from e-wastes.

6. Conclusions

Based on the laboratory scale studies following conclusions have been made for the recovery of metals in the form of pure metallic sheets as discussed below.

* High purity Cu (Purity: 99.99%) was obtained from the metal leach solution of e-waste using electro-winning technique at a current density of 200-212 A/m^2 with 93.5% current efficiency using Pb as anode and Ti as a cathode.

* Similarly, 99.99% pure Ni sheet was obtained between current density 200 to 220 m/A^2 with current efficiency of more than 85% at 60 ^oC in the pH range of 3 to 3.5.

* Further, 99.99% pure Co was deposited on the cathode at current density 200-205 m/A^2 with current efficiency of 90% in the pH range of 3.8 to 4.2 between 60-70 ^oC.

· Subsequently, Mn was deposited as electrolytic manganese dioxide (EMD) powder in the bag of cathode at current density of 160 A/m^2 in the temperature range of 60-65 ^oC.

Acknowledgement

Authors are thankful to Director, CSIR-National Metallurgical Laboratory, Jamshedpur, India for giving permission to publish this paper.

References

1. Yang, J.; Wang, H.; Zhang, G.; Bai, X.; Zhao, X.; He, Y. Recycling organics from non-metallic fraction of waste printed circuit boards by a novel conical surface triboelectric separator. Resour. Conserv. Recycl. **2019**, 146, 264–269.

2. Forti, V.; Balde, C.P.; Kuehr, R.; Bel, G. The Global E-Waste Monitor 2020: Quantities, Flows and the Circular Economy Potential; United Nations University (UNU)/United Nations Institute for Training and Research (UNITAR)—Co-hosted SCYCLE Programme, International Telecommunication Union (ITU) & International Solid Waste Association (ISWA): Bonn, Germany; Geneva, Switzerland; Rotterdam, The Netherlands, **2020**.

3. Jin,W.; Hu, M.; Hu, J. Selective and Efficient Electrochemical Recovery of Dilute Copper and Tellurium from Acidic Chloride Solutions. ACS Sustain. Chem. Eng. **2018**, 6, 13378–13384.

4. Rai, V.; Tiwari, N.; Rajput, M.; Joshi, S.; Nguyen, A.C.; Mathews, N. Reversible Electrochemical Silver Deposition over Large Areas for Smart Windows and Information Display. Electrochim. Acta **2017**, 255, 63–71.

5. Rai, V.; Toh, C.-S. Electrochemical Amplification Strategies in DNA Nanosensors. Nanosci. Nanotechnol. Lett. **2013**, 5, 613–623.

6. Clevenger, T.E.; Novak, J.T. Recovery of Metals from ElectroplatingWastes Using Liquid-Liquid Extraction. J.Water Pollut. Control Fed. **1983**, 55, 984–989.

7. Deng, S.; Zhang, D.; Zhou, J.; Liu, H. Recycling of waste printed circuit board and preparation of high strength high purity copper foil by electrochemical method. Xiyou Jinshu/Chin. J. Rare Met. **2016**, 40, 914–921.

8. Ghosh, B.; Ghosh, M.; Parhi, P.; Mukherjee, P.; Mishra, B. Waste Printed Circuit Boards recycling: An extensive assessment of current status. J. Clean. Prod. **2015**, 94, 5–19.

9. Kim, E.Y.; Kim, M.S.; Lee, J.C.; Jha, M.K.; Yoo, K.K.; Jeong, J. Effect of cuprous ions on Cu leaching in the recycling of waste PCBs, using electro-generated chlorine in hydrochloric acid solution. Miner. Eng. **2008,** 21, 121–128.

10. Choubey, P.K.; Lee, J.C.; Kim, M.S.; Kim, H.S. Conversion of chalcopyrite to copper oxide in hypochlorite solution for selective leaching of copper in dilute sulfuric acid solution. Hydrometallurgy 2018, 178, 224-230.

11. Zhang, C.; Lu, J.; Krof, A.J.; Wu, T.; Jansen, A.N.; Sun, Y.K.; Qiu, X.; Amine, K. Mn(II) deposition on anodes and its effects on capacity fade in spinel lithium manganate–carbon systems. Nature communication, **2013**, 2437.

12. https://byjus.com/chemistry/reactivity-series/